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COMPLETE SPECIFICATION

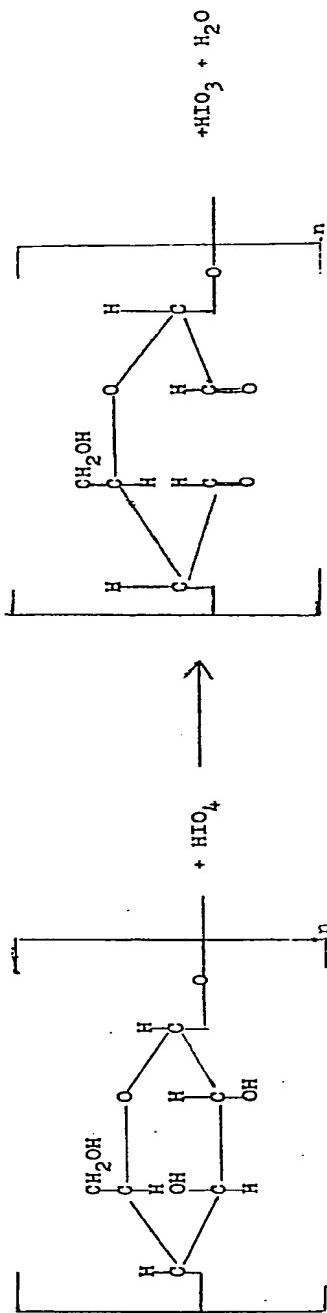
Dialdehyde Polysaccharide Compositions

We, MILES LABORATORIES INC., a corporation organised and existing under the laws of the State of Indiana, United States of America, of 1127 Myrtle Street, Elkhart, Indiana, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a form of dialdehyde polysaccharide which is soluble in water at room temperature and to a process of preparing such material. More particularly, this invention relates to a spray dried reaction product of a dialdehyde polysaccharide and a hypochlorite oxidized polysaccharide or a condensation product of dicyandiamide and formaldehyde or a mixture of the oxidized polysaccharide and the condensation product.

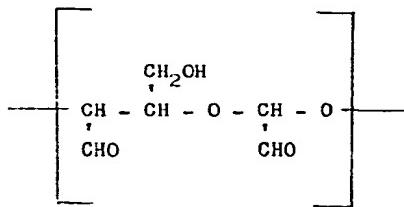
Dialdehyde polysaccharides are well known in the art. Such materials are frequently referred to as periodate oxidized polysaccharides because of their preparation by the well known oxidation of polysaccharides with periodic acid. This preparation can be illustrated by the conversion of a polysaccharide, such as starch, to dialdehyde starch or periodate oxidized starch using periodic acid in accordance with the following equation:

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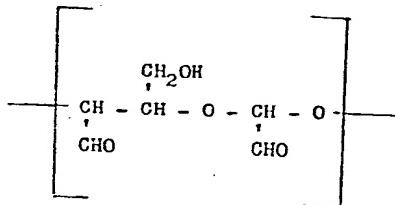
wherein n stands for the number of repeating structural units in the molecule, which may range from as few as about 20 to as many as several thousand. The preparation of dialdehyde starch is more particularly described in U.S. Patents No. 2,648,629 and 2,713,553. It is also known that the dialdehyde polysaccharides are quite insoluble in water, especially cold water or water at room temperature. Since these materials are generally employed in aqueous applications, they must be appreciably dissolved or intimately dispersed in aqueous media. Various techniques have been employed in the prior art to disperse the dialdehyde polysaccharides and thus increase their water solubility. It is also known that dialdehyde polysaccharides are useful to improve the wet tensile strength of cellulosic paper. However, a cationizing or coupling agent must be employed to aid in bonding the dialdehyde polysaccharide to the paper or paper pulp. These cationizing agents can be added to the paper or paper pulp prior to contacting the treated paper or the paper pulp with an aqueous dispersion of dialdehyde polysaccharide. Alternatively, the aqueous dispersion of the dialdehyde polysaccharide can be mixed with the cationizing agent prior to contacting the paper or paper pulp. In either case the difficult step of first dispersing the dialdehyde polysaccharide must be completed before contact with the cationizing agent can be made. Such prior art techniques have the disadvantage of requiring a separate cationizing agent with the attendant supply and mixing problems.

We have found a form of dialdehyde polysaccharide which is readily soluble in water at room temperature and which, in some aspects of the invention, does not require a separate cationizing agent. Accordingly the present invention provides a composition dispersible in water at room temperature comprising the finely divided solidified reaction product of from 70 to 85 parts by weight of a dialdehyde polysaccharide in which from 0.5 to 100 units of each original 100 units of anhydroglucose units of the polysaccharide have been oxidised to dialdehyde units represented by the formula



with from 15 to 30 parts by weight of a condensation product of dicyandiamide and formaldehyde or from 15 to 30 parts by weight of a hypochlorite oxidized polysaccharide or with a mixture of 7.5 to 15 parts by weight of the condensation product and from 7.5 to 15 parts by weight of the hypochlorite oxidized polysaccharide.

One class of the novel compositions of the present invention comprises the finely divided solidified reaction products of from 70 to 85 parts by weight dialdehyde polysaccharide wherein from 0.5 to 100 units out of each 100 of the original anhydroglucose units of the polysaccharide have been oxidized to dialdehyde units represented by the formula:



with from 7.5 to 15 parts by weight of hypochlorite oxidized polysaccharides, and from 7.5 to 15 parts by weight of a condensation product of dicyandiamide and formaldehyde. Preferably the compounds of the present invention are formed from dialdehyde polysaccharides which are from 90 to 100 percent oxidized. The preferred compounds contain 70 parts by weight dialdehyde polysaccharides, 15 parts by weight hypochlorite oxidized polysaccharides and 15 parts by weight of a condensation product of dicyandiamide and formaldehyde. In addition, the preferred finely divided solidified products are spray-dried.

This first class of composition can be prepared by mixing in water 70 to 85 parts by weight, preferably 70 parts by weight, dialdehyde polysaccharides, from 7.5 to 15 parts by weight, preferably 15 parts by weight, hypochlorite oxidized polysaccharides and from 7.5 to 15 parts by weight preferably 15 parts by weight, of a condensation product of dicyandiamide and formaldehyde to form a slurry containing 15 to 25 weight percent solids, heating the slurry with stirring to 90 to 100° C., maintaining the slurry at 90 to 100° C. with stirring for 5 to 15 minutes until the dispersion of the solid material is complete, cooling the dispersion to 70° C., adjusting the pH of the dispersion to 4 to 5.5 and then drying the dispersion, preferably by spray-drying, and collecting the finely divided solidified product. Preferably the dispersion temperature is 95 to 97° C. Preferably the pH of the dispersion is adjusted to 4.3 to 4.5 before spray-drying. If the highly acid dispersion obtained by the above process is not adjusted to the above proper pH values before spray-drying, the resulting spray-dried solid product is not easily redispersible in water at room temperature. The pH is adjusted by well-known techniques, such as adding minor amounts of sodium hydroxide, sodium carbonate, borax and dibasic sodium phosphate. Typical spray-drying techniques and apparatus are employed in spray-drying the above prepared dispersion. The alkalinity of the water employed to prepare the dispersions is not critical in the present invention whereas the prior art dispersion processes were quite sensitive as to the alkalinity of the water.

Another class of the novel compositions provided by the invention comprises the finely divided solidified reaction product of from 15 to 30 parts by weight hypochlorite oxidized polysaccharides and from 70 to 85 parts by weight dialdehyde polysaccharides wherein from 0.5 to 100 units out of 100 of the original anhydroglucose units of the original polysaccharides have been oxidized to dialdehyde units as defined above. The

preferred compounds contain 70 parts by weight dialdehyde polysaccharides and 30 parts by weight hypochlorite oxidized polysaccharides.

The second class of novel compositions can be prepared by mixing 70 to 85 parts by weight, preferably 70 parts by weight, dialdehyde polysaccharides with from 15 to 30 parts by weight, preferably 30 parts by weight, hypochlorite oxidized polysaccharides in water to form a slurry containing 10 to 15 weight percent solids, heating the slurry to 90° to 100° C., preferably 95 to 97° C., for 5 to 15 minutes with stirring until the dispersion of the solid material is complete, cooling the dispersion to 70° C., adjusting the pH of the dispersion to 4 to 5.5; preferably 4.3 to 4.5, and then drying the dispersion, preferably by spray-drying, and collecting the finely divided dried solidified product. If the dispersion obtained by the above process is not adjusted to the proper pH value before spray-drying, the resulting finely divided solid product is not easily redispersible in water at room temperature. The pH is adjusted by well-known techniques, such as adding minor amounts of sodium hydroxide, sodium carbonate, borax, dibasic sodium phosphate and the like.

A further class of novel compositions provided by the invention comprise the finely divided solidified reaction products of 15 to 30, preferably 15 to 25, parts by weight of a condensation product of dicyandiamide and formaldehyde and 70 to 85, preferably 75 to 85 parts by weight dialdehyde polysaccharides wherein from 0.5 to 100 units out of 100 of the original anhydroglucose units of the original polysaccharides have been oxidized to dialdehyde units as defined above. Preferably the compounds of the present invention are formed from dialdehyde polysaccharides which are from 90 to 100 percent oxidized. Some suitable compounds contain 70 parts by weight dialdehyde polysaccharides and 30 parts by weight of a condensation product of dicyandiamide and formaldehyde.

The third class of novel compositions are prepared by the novel process of mixing 70 to 85, preferably 75 to 85 parts by weight dialdehyde polysaccharides with 15 to 30, preferably 15—25 parts by weight condensation product of dicyandiamide and formaldehyde in 300 to 500 parts by weight water to form a slurry containing 20 to 30 weight percent solids, heating the slurry with stirring to 70 to 100° C., maintaining the slurry at 70 to 100° C. with stirring for 10 to 15 minutes until the dispersion of the solid material is complete, cooling the dispersion to 70° C., adjusting the pH of the dispersion to 4 to 5.5 and then drying the dispersion preferably by spray-drying and collecting the finely divided dried solidified product. Preferably the dispersion temperature is 85—95° C.

Preferably the pH of the dispersion is adjusted to 4.3 to 4.5 before spray-drying. If the highly acid dispersion obtained by the above process is not adjusted to the above proper pH values before spray-drying, the resulting finely divided solid product is not easily redispersible in water at room temperature.

The dialdehyde polysaccharides to be used as starting materials to prepare the novel compounds of the present invention may be the dialdehyde derivatives of any polysaccharide, such as corn, wheat, rice, tapioca or potato starches, amyloses, amylopectins, celluloses and gums. Of these polysaccharides, the dialdehyde derivatives of starch known generically as dialdehyde starch are the best known and most widely used. However, where it is desired to have dialdehydes of other polysaccharides, these may be used as well. The dialdehyde polysaccharides used in the present invention can be from 0.5 to 100 percent oxidized, i.e. those wherein 0.5 to 100 of each 100 of the original anhydroglucose units have been converted to dialdehyde units such as by periodate oxidation as above described. In general, it is preferred to use dialdehyde polysaccharide derivatives which are from 90 percent to 100 percent oxidized.

The hypochlorite oxidized polysaccharides to be used as starting materials to prepare the novel compounds of the present invention are well-known in the art and are prepared by well-known procedures, such as treatment of starches with alkaline hypochlorite salts.

The condensation products of dicyandiamide and formaldehyde used as starting materials in preparing the novel compounds of the present invention are well-known in the art. Generally such condensation products are prepared by mixing dicyandiamide, formaldehyde and a catalyst, such as ammonium chloride, and allowing the exothermic reaction to heat the mixture to 65 to 100° C. The dicyandiamide-formaldehyde condensation product preferably employed in the present invention is prepared by forming an aqueous slurry of from 1.5 to 2.0 moles of formaldehyde and 1 mole of dicyandiamide, adding stepwise to the slurry 0.3 to 0.6 moles of a catalyst, such as ammonium chloride, in amounts to maintain the temperature of the reaction mixture below 70° C. and to maintain the pH of the reaction mixture initially between 1.0 and 2.5 and upon

completion of the reaction between 2.5 and 3.5, carrying out the reaction at a temperature below 70° C. and pH below 3.5 until a water-soluble reaction product having an average molecular weight of 500 to 700 is obtained, and then cooling the reaction product to room temperature. Upon standing at room temperature the pH of the reaction mixture will gradually increase within 2 hours to 3.8 to 4.2.

The dialdehyde polysaccharide products of the present invention are substantially free-flowing powder which are easily dispersed by simple mixing in water at room temperature. The alkalinity of the water is not critical but the pH of the final dispersion is preferably 4.5 to 5.0. In addition when the condensation product of di-cyandiamide and formaldehyde is included the resulting dispersions are cationic and readily couple to paper or paper pulp to aid in improving the dry and wet tensile strengths of the so-treated paper or paper resulting from the treated paper pulp. These powder products are a distinct improvement over solidified dialdehyde polysaccharides obtainable in the prior art since the prior materials were not *per se* dispersible in water at room temperature and were not *per se* cationic.

The process of the present invention is also a distinct improvement over the prior art since higher solids content can be employed in the dialdehyde polysaccharide slurry without gel formation. The time at dispersion temperature of 5 to 15 minutes is substantially less than the 40 minutes generally used by the prior art to disperse the dialdehyde polysaccharides alone. This feature enables the dispersion process, which was a batch technique in the prior art, to become a substantially continuous process, if desired. The present process has an additional advantage. When the reaction mixture slurry is heated to dispersion temperature, the dialdehyde polysaccharides and the hypochlorite oxidized polysaccharides pass directly from the solid phase to a liquid dispersed phase without passing through a swelling phase. The lack of swelling, which is always present with prior art dialdehyde polysaccharide materials, enables equipment of smaller volume to be used for dispersion.

When the products of the second class of compounds of the present invention are redispersed in water and are to be used to treat paper or paper pulp so as to improve the dry and wet tensile strengths of the resulting treated paper, it is generally necessary to also employ a cationizing agent to aid in coupling the dispersed reaction product to the paper or paper pulp. These cationizing agents are well-known cationic starches, polymeric amines and polyamides. The cationizing agent can be added first to paper or a slurry of paper pulp, followed by addition of the reaction product dispersion. Alternatively, the cationizing agent and the reaction product dispersion can be mixed together and this mixture applied to the paper or paper pulp. Illustrative examples of useful cationizing agents are condensation products of dicyandiamide and formaldehyde and water-soluble polyamide resins crosslinked with epichlorohydrin.

The invention is further described in the following examples.

EXAMPLE I.

To a 30 litre stainless steel kettle fitted with a steam and water jacket were charged 20 litres of tap water and 0.6 kg. of dicyandiamide-formaldehyde condensation product prepared in accordance with the preferred procedure described. This mixture was stirred about 3 minutes. To this were then added 2.8 kg. of dialdehyde corn starch (containing 9 to 10 weight percent moisture and about 90—98 percent oxidized) and 0.6 kg. of hypochlorite oxidized corn starch (Douglas Clearsol Gum, Grade W, sold by Penick & Ford, Ltd). The resulting slurry was stirred for about 3 minutes. The reactants were employed in the ratio of 70 weight parts dialdehyde starch, 15 weight parts hypochlorite oxidized starch and 15 weight parts condensation product of di-cyandiamide and formaldehyde. Steam was then introduced to the kettle jacket and the stirring was continued. In about 10 minutes the slurry reached the desired temperature of 95° C. The temperature was maintained at this value for 15 minutes after which time the dispersion was complete. The dispersion was then cooled to about 70° C., the pH adjusted to 4.3 and then passed into a spray-drier having an inlet temperature of about 177° C. and 77° C. outlet temperature. The spray-dried product was collected in plastic bags.

The utility of the above product is shown in the following example.

EXAMPLE II.

A 50 g. portion of the product obtained in Example I was added to 950 ml. of distilled water at 26 to 28° C. and stirred until the finely divided material was thoroughly dispersed or dissolved (about 15 minutes). A portion of this cationic dispersion was added to a bleached cellulosic Kraft pulp beaten to a Canadian Standard

5 Freeness of 450 cc. and which had been diluted to a consistency of 1.0 weight percent based on oven dry pulp. The cationic dispersion was added in an amount of 1.0 weight percent solids based on oven dry pulp. Handsheets having a basis weight of 40 lbs. for 500 sheets 24 x 36 in. were prepared from this pulp on standard equipment, such as
 10 a Noble and Wood handsheet machine. These handsheets were conditioned at 21 to 23° C. for 24 hours at 50±3 percent relative humidity. Test strips cut from these handsheets were then soaked in water at room temperature for 5 minutes and the wet tensile strength was measured by well-known techniques. The test procedure is described in TAPPI standard T 456 m-49. The wet tensile strength was 8.5 lbs/in.
 15 of width. Handsheets having the same basis weight but containing none of the cationic dispersion had wet tensile strength values of only about 1.76 lbs/in. of width. Tap water can also be used for forming the dispersion without affecting the tensile strength of the resulting treated paper.

EXAMPLE III.

15 Handsheets were prepared according to the procedures of Example II above. Test strips cut from these handsheets were then tested for dry tensile strength according to TAPPI standard T 404 os-61. Handsheets containing the cationic dispersion had dry tensile strength of 29.2 lbs/in. width while handsheets which did not contain the cationized dispersion had dry tensile strength of only 24.6 lbs/in. width.

20 EXAMPLE IV.

To a 30 litre stainless steel kettle fitted with a steam and water jacket were charged 22.0 litres of tap water and 0.75 kg. of a dicyandiamide-formaldehyde condensation product prepared in accordance with the preferred procedure described. The mixture was stirred for about 3 minutes. Dialdehyde corn starch (4.25 kg.) containing 9 to 10 weight percent moisture and about 90 to 98 percent oxidized was then added and the resulting slurry was stirred for about 3 minutes. The reactants were employed in the ratio of 85 weight parts dialdehyde starch to 15 weight parts of the condensation product. Steam was then introduced to the kettle jacket and the stirring was continued. In about 10 minutes the slurry reached the desired temperature of 95° C. The temperature was maintained at this value. A very thick gel formed after 2 minutes at 95° C. and this gel remained for an additional 2 minutes. After about 6 to 10 minutes, the dispersion was complete. The dispersion was then cooled to about 70° C., the pH adjusted to 4.3 to 4.5 and then passed into a spray-drier having an inlet temperature of about 177° C. and 77° C. outlet temperature. The cationic spray dried product was collected in plastic bags.

The utility of the above product is shown in the following example.

EXAMPLE V.

40 A 50 g. portion of the product obtained in Example IV was added to 1000 ml. of distilled water at 26 to 28° C. and stirred until the finely divided material was thoroughly dispersed or dissolved (about 15 min.). A portion of this dispersion of cationic dialdehyde starch was added to a bleached Kraft cellulosic pulp having a Canadian Standard Freeness of 525 ml. and which had been diluted to a consistency of 1.0 weight percent base on oven dry pulp. The cationic dialdehyde starch was added in an amount of 1 weight percent based on oven dry-pulp. Handsheets of this so-treated pulp were prepared on standard equipment, such as a Noble and Wood handsheet machine. These handsheets were conditioned at 22±1° C. for 24 hours at 50±3 percent relative humidity. Test strips cut from these handsheets were then soaked in distilled water at room temperature for 5 minutes and the wet tensile strength was measured by well-known techniques. The procedure followed is described in TAPPI standard T 456 m-49. The wet tensile strength was 7.51 lbs/in. of width. Handsheets having the same basis weight (40 lbs. for 500 sheets, 24 x 36 in.) but containing none of the above described cationic dialdehyde starch had wet tensile strength values of only about 1.82 lbs/in. of width. Increasing the dispersing time from 15 min. to 60 min. did not have any appreciable effect on the wet tensile strength of paper made from pulp treated with the cationic dialdehyde starch dispersion. Tap water can also be used for forming the dispersion without affecting the wet tensile strength of the resulting paper.

EXAMPLE VI.

60 A reaction product was obtained by the method described in Example I by mixing in a water slurry 80 parts by weight of dialdehyde corn starch described in Example IV and 20 parts by weight of a condensation product of dicyandiamide and formaldehyde prepared in accordance with the preferred procedure described. The spray-

5 dried product of this reaction was readily dispersed in distilled water at room temperature and the dispersion employed to treat paper pulp and prepare cellulosic handsheets as described in Example II. The resulting handsheets had wet tensile strength of about 5.21 to 5.79 lbs./in. of width. Dispersing times of 15 to 60 min. at 26 to 27° C. were
5 employed for the cationic dialdehyde starch added to the paper pulp.

10 EX-EXAMPLE VII.
A reaction product was obtained by the method described in Example I by mixing in a water slurry 75 parts by weight of dialdehyde corn starch described in Example IV and 25 parts by weight of a dicyandiamide-formaldehyde condensation product prepared in accordance with the preferred procedure described. The spray-dried product of this reaction was dispersed in distilled water at 26 to 27° C. with dispersing time of 15 to 60 min., and the dispersion was employed to treat paper pulp and prepare cellulosic handsheets as described in Example II. The resulting handsheets had wet tensile strength of about 5.88 to 5.90 lbs./in. of width.

15 It can be seen from the above examples that the finely divided solid product of the present invention can readily be dispersed in water at room temperature by simple mixing, and that the resulting cationic dispersion is useful in improving the wet tensile strength of paper.

20 The finely divided dry product of the present invention is also quite stable upon storage. It has been stored at room temperature and 48±3 percent relative humidity for 10 to 20 days and the stored product could still easily disperse in room temperature water. A dispersion of dialdehyde starch in water begins to form a gel and thus becomes unstable after 10 to 20 days storage.

25 Use of the product of the present invention for treating paper or paper pulp also results in improved dry strength properties of the treated paper. This is shown in the following example.

30 EX-EXAMPLE VIII.
A reaction product was obtained as described in Example IV. The spray-dried product was readily dispersed in distilled water at room temperature and the dispersion employed to treat paper pulp and prepare handsheets as described in Example II. The paper pulp was a northern bleached cellulosic Kraft having a Canadian Standard Freeness of 410 cc. Samples of handsheets having the same basis weight (40 lbs/ream of 500 sheets, 24 x 36 in.) were also prepared wherein no cationic dialdehyde starch treatment was employed. Properties of the paper prepared both with and without cationic dialdehyde starch were then compared. The results are shown in the following table.

TABLE I

Weight Percent Cationic Dialdehyde Starch.	Dry ⁽¹⁾ Tensile Strength, lbs/in. width	Dry ⁽²⁾ Bursting Strength, lbs/sq.in. area	Folding ⁽³⁾ Endurance, Schopper Double Folds.
0	13.1	57.5	610
1.0	19.6	100	1550

(¹) TAPPI Standard T 404 os-61.

(²) TAPPI Standard T 403 m-53

(³) TAPPI Standard T 423 m-50

EXAMPLE IX.

40 Seventy (70) grams of a dialdehyde corn starch (containing 9 to 10 weight percent moisture and about 90 to 98 percent oxidized) plus 30 grams of hypochlorite oxidized corn starch (Douglas Clearsol Gum Grade W., sold by Penick & Ford, Ltd.) were mixed together and added to 900 ml. of tap water at 95° C. This mixture required 5 minutes to disperse. This dispersion was then cooled to 70° C., pH adjusted to 4.3

and then passed into a spray-drier having an inlet temperature of about 177° C. and 77° C. outlet temperature. The spray dried product was collected in plastic bags. The utility of the above product is shown in the following example.

EXAMPLE X.

5 A 50 g. portion of the product obtained in Example IX was added to 950 ml. of tap water at 26 to 28° C. and stirred for about 10 minutes at which time the finely divided material was thoroughly dispersed or dissolved. To this dispersion were added 10 g. of zirconium oxychloride as a cationizing agent. A portion of this cationized 10 dispersion was added to a bleached cellulosic Kraft pulp having 450 cc. Canadian standard Freeness and which had been diluted to a consistency of 1.0 weight percent based on oven dry pulp. The cationized dispersion was added in an amount of 1.0 weight percent solids based on oven dry pulp. Handsheets having basis weight of 40 lbs. for 500 sheets 24 x 36 in. were prepared from this pulp on standard equipment, such as a Noble and Wood handsheet machine. These handsheets were conditioned at 15 21 to 23° C. for 24 hours at 50±3 percent relative humidity. Test strips cut from the handsheets were then soaked in water at room temperature for various periods of time and then tested for wet tensile strength. The test procedure is described in TAPPI standard T 456 m-49. Some of the handsheets were stored and aged for several days at 21 to 23° C. (72±2° F.) and 50±3 percent relative humidity before 20 testing for wet/tensile strength. The test results are tabulated below. Handsheets of same basis weight which were not treated with the novel reaction product had wet tensile strength of only 1.80 lbs/in. width.

TABLE II

Soaking Time Min.	Ageing Days	Wet Tensile Strength lbs/in. of width
0	0	8.8
5	0	7.74
30	0	6.50
60	0	5.30
180	0	4.7
5	3	9.1
5	7	10.6

25 It can be seen from the above data that the use of the novel reaction product of the present invention provides improved wet tensile strength for paper. It is also seen that ageing of the treated paper for several days provides additional improvement in wet tensile strength. Similar increases in wet tensile strength values can be obtained by ageing at 105° C. for 10 minutes, for example.

EXAMPLE XI.

30 Handsheets having a basis weight of 40 lbs. for 500 sheets 24 x 36 in. were prepared from bleached Kraft pulp beaten to 540 cc. Canadian Standard Freeness which had been mixed with dispersions of 1.0 weight percent dialdehyde starch, 0.7 weight percent dialdehyde starch and the reaction product containing 0.7 weight percent dialdehyde starch and 0.3 weight percent hypochlorite oxidized starch, respectively. Test strips cut from the handsheets were soaked in distilled water at room temperature for 35 5 minutes and then the wet tensile strength were measured. The results are shown in the following table.

TABLE III

Dialdehyde Starch	Starch Dispersion Weight Percent	Wet Tensile Strength lbs./in. of width
	Hypochlorite Oxidized Starch	
1.0	—	7.8
0.7	—	6.2
0.7	0.3	8.4

It can be seen from the above data that the reaction product of hypochlorite oxidized starch and dialdehyde starch is useful in increasing the wet tensile strength of so-treated paper.

EXAMPLE XII.

Handsheets having a basis weight of 40 lbs. for 500 sheets 24×36 in. were prepared from bleached cellulosic Kraft pulp beaten to Canadian Standard Freeness of about 450 cc. Handsheets were also prepared from this pulp which had been mixed with 1.0 weight percent, based on oven dry pulp, of the dialdehyde starch-hypochlorite oxidized starch reaction product of Example IX. Portions of both pulps were aged at room temperature for seven days and handsheets were then prepared from the aged pulps. Dry tensile strengths were measured on test strips cut from these handsheets according to TAPPI Standard T 404 os-61. The results are tabulated below.

TABLE IV.

Dialdehyde Starch	Dispersion, weight percent	Oxidized Starch	Ageing Days	Dry Tensile Strength lbs./in. of width
0	0	0	0	23.4
0.7	0.3	0.3	0	26.8
0	0	0	7	23.6
0.7	0.3	0.3	7	28.2

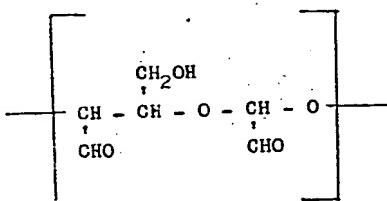
EXAMPLE XIII.

To a 100 gallon stainless steel kettle fitted with a steam and water jacket and an anchor type agitator were charged 523 lb. of tap water having an alkalinity of 100 ppm. Also added were 78.5 lb. of an aqueous dispersion containing 60 weight percent of a dicyandiamide-formaldehyde condensation product prepared in accordance with the above described preferred procedure. The kettle contents were then agitated for 5 minutes. Moisture-free dialdehyde corn starch (108 lb.) being about 90 to 98 percent oxidized was then added and the kettle contents agitated for 5 minutes while being heated to 180° F. (82° C.). The reactants were employed in the relative amounts of 70 weight parts of dialdehyde starch and 30 weight parts of the condensation product. The steam was then turned off and agitation was continued for 30 minutes. The dispersion had been completed within 10 to 15 minutes. The kettle contents were then cooled to 160° F. (71° C.), the pH adjusted to 4.2 to 4.4 and then passed into a spray-drier having an inlet temperature of about 177° C. and an outlet temperature of about 77° C. The resulting cationic spray dried product was collected in fibre-board containers.

The spray-dried reaction product prepared above was readily dispersed in distilled water at room temperature (19° C) to form an aqueous dispersion containing 12 weight percent of the cationic reaction product. A portion of this dispersion of cationic dialdehyde starch reaction product, after standing for 1 hour, was added to an unbleached Kraft cellulosic pulp having a Canadian Standard Freeness of 450 ml. and which had been diluted to a consistency of 0.5 weight percent based on oven dry pulp. The pH of the pulp had been adjusted to 4.5 with dilute sulphuric acid. The cationic dialdehyde starch reaction product was added in an amount of 1 weight percent based on oven dry pulp. Handsheets of this so-treated pulp were prepared on standard equipment, such as a Noble and Wood handsheet machine. Test strips cut from these handsheets were then soaked in distilled water at room temperature for 5 minutes and the wet tensile strength was measured in accordance with TAPPI Standard T456 M-49. The wet tensile strength was 9.29 lbs./in. of width. Handsheets having the same basis weight (40 lbs. for 500 sheets, 24×36 in.) but containing none of the above described cationic product had wet tensile strength values of only about 1.60 lbs./in. of width. Test strips which were not soaked in water were tested for dry tensile strength according to TAPPI Standard T404 os-61. The handsheets containing the cationic dialdehyde starch reaction product had dry tensile strength of 38.74 lbs./in. of width while prior art handsheets had dry tensile strengths of only about 34.22 lbs./in. of width.

WHAT WE CLAIM IS:—

1. A composition dispersible in water at room temperature comprising the finely divided solidified reaction product of from 70 to 85 parts by weight of a dialdehyde polysaccharide in which from 0.5 to 100 units out of each original 100 units of anhydroglucose units of the polysaccharide have been oxidised to dialdehyde units represented by the formula



with from 15 to 30 parts by weight of a condensation product of dicyandiamide and formaldehyde or with from 15 to 30 parts by weight of a hypochlorite oxidised polysaccharide or with a mixture of 7.5 to 15 parts by weight of the condensation product and from 7.5 to 15 parts by weight of the hypochlorite oxidized polysaccharide.

2. A composition as claimed in claim 1 comprising the finely-divided solidified reaction product of from 70 to 85 parts by weight of a dialdehyde polysaccharide in which from 0.5 to 100 units out of 100 of the original anhydroglucose units of the polysaccharide have been oxidized to dialdehyde units as represented by the formula defined in claim 1, with from 7.5 to 15 parts by weight hypochlorite oxidized polysaccharides, and from 7.5 to 15 parts by weight of a condensation product of dicyandiamide and formaldehyde.

3. A composition as claimed in claim 1 comprising the finely-divided solidified reaction product of from 15 to 30 parts by weight hypochlorite oxidized polysaccharide and from 70 to 85 parts by weight dialdehyde polysaccharide wherein from 0.5 to 100 units out of 100 of the original anhydroglucose units of the original polysaccharides have been oxidized to dialdehyde units as defined in claim 1.

4. A composition as claimed in claim 1 comprising the finely-divided solidified reaction product of 15 to 30 parts by weight of a condensation product of dicyandiamide and formaldehyde and 70 to 85 parts by weight dialdehyde polysaccharide wherein from 0.5 to 100 units out of 100 of the original anhydroglucose units of the original polysaccharide have been oxidized to dialdehyde units as defined in claim 1.

5. A composition as claimed in claim 1 comprising the finely-divided solidified reaction product of 15 to 25 parts by weight of a condensation product of dicyandiamide and formaldehyde and 75 to 85 parts by weight dialdehyde polysaccharides wherein from 0.5 to 100 units out of 100 of the original anhydroglucose units of the original polysaccharide have been oxidized to dialdehyde units as defined in claim 1.

6. A composition as claimed in any of the preceding claims wherein from 90 to 100 units out of the 100 of the original anhydroglucose units of the polysaccharide have been oxidized to dialdehyde units as defined in claim 1.

7. A composition as claimed in any of the preceding claims which has been solidified by spray-drying.
8. A composition as claimed in claim 1 substantially as described with reference to any of Examples I to III.
- 5 9. A composition as claimed in claim 1 substantially as described with reference to any of Examples IV to VIII.
- 10 10. A composition as claimed in claim 1 substantially as described with reference to any of Examples IX to XII.
- 10 11. Cellulosic paper having improved strength properties, which paper has been treated with an aqueous dispersion of a composition as claimed in any of the preceding claims.
- 15 12. A process for preparing a composition as claimed in claim 2 which comprises mixing in water from 70 to 85 parts by weight dialdehyde polysaccharides, from 7.5 to 15 parts by weight hypochlorite oxidized polysaccharides and from 7.5 to 15 parts by weight of a condensation product of dicyandiamide and formaldehyde to form a slurry containing 15 to 25 weight percent solids, heating the slurry with stirring to a temperature of from 90° to 100° C. for 5 to 15 minutes until the dispersion of the solid material is complete, cooling the dispersion to 70° C., adjusting the pH of the dispersion to 4 to 5.5 and then drying the dispersion and collecting the finely-divided solidified product.
- 20 13. A process for preparing a composition as claimed in claim 3 which comprises mixing in water from 70 to 85 parts by weight dialdehyde polysaccharides with from 15 to 30 parts by weight hypochlorite oxidized polysaccharides to form a slurry containing 10 to 15 weight percent solids, heating the slurry to a temperature of from 90° to 100° C. for 5 to 15 minutes with stirring until the dispersion of the solid material is complete, cooling the dispersion to 70° C., adjusting the pH of the dispersion to 4 to 5.5 and then drying the dispersion and collecting the finely-divided dried solidified product.
- 25 14. A process for preparing a composition as claimed in claim 4 which comprises mixing in water 70 to 85 parts by weight dialdehyde polysaccharides with 15 to 30 parts by weight condensation product of dicyandiamide and formaldehyde to form a slurry containing 20 to 30 weight percent solids, heating the slurry with stirring to a temperature of from 70° to 100° C., maintaining the slurry at 70° to 100° C. with stirring for 10 to 15 minutes until the dispersion of the solid material is complete, cooling the dispersion to about 70° C., adjusting the pH of the dispersion to 4 to 5.5 and then drying the dispersion and collecting the finely-divided dried solidified product.
- 30 15. A process for preparing a composition as claimed in claim 5 which comprises mixing in water 75 to 85 parts by weight dialdehyde polysaccharides with 15 to 25 parts by weight condensation product of dicyandiamide and formaldehyde to form a slurry containing 20 to 30 weight percent solids, heating the slurry with stirring to 70 to 100° C., maintaining the slurry at 70 to 100° C. with stirring for 10 to 15 min. until the dispersion of the solid material is complete, cooling the dispersion to about 70° C., adjusting the pH of the dispersion to 4 to 5.5 and then drying the dispersion and collecting the finely-divided dried solidified product.
- 35 16. A process as claimed in any of claims 12 to 15 wherein the pH of the dispersion is adjusted to 4.3 to 4.5 before drying.
17. A process as claimed in any of claims 12 to 16 wherein the dispersion is dried by spray drying.
- 50 18. A process as claimed in any of claims 12, 13 or 15 wherein the dispersion temperature is 95° to 97° C.
19. A process as claimed in claim 14 wherein the dispersion temperature is 85 to 95° C.
- 55 20. A process as claimed in claim 15 wherein 85 parts by weight dialdehyde polysaccharides are mixed with 15 parts by weight of condensation product of dicyandiamide and formaldehyde.
- 60 21. A process as claimed in claim 13 which comprises mixing in water 70 parts by weight dialdehyde polysaccharides with 30 parts by weight hypochlorite oxidized polysaccharides to form a slurry containing 10 to 15 weight percent solids, heating the slurry to 95° to 97° C. for 5 to 15 minutes with stirring until the dispersion of the solid material is complete cooling the dispersion to 70° C., adjusting the pH of the dispersion to 4.3 to 4.5 and then spray drying the dispersion and collecting the finely-divided dried solidified product.
- 65 22. A process as claimed in claim 12 which comprises mixing in water 70 parts by weight dialdehyde polysaccharides, 15 parts by weight hypochlorite oxidized poly-

5 saccharides and 15 parts by weight of a condensation product of dicyandiamide and formaldehyde to form a slurry containing 15 to 25 weight percent solids, heating the slurry with stirring to 95° to 97° C. for 5 to 15 minutes until the dispersion of the solid material is complete, cooling the dispersion to 70° C., adjusting the pH of the dispersion to 4.3 to 4.5 and then spray drying and collecting the finely-divided dried solidified product.

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10 23. A process as claimed in claim 14 wherein 70 parts by weight dialdehyde polysaccharides are mixed with 30 parts by weight of condensation product of dicyandiamide and formaldehyde.

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15 24. A process as claimed in claim 14 which comprises mixing in water 70 parts by weight dialdehyde derivatives of polysaccharides with 30 parts by weight condensation product of dicyandiamide and formaldehyde to form a slurry containing 20 to 30 weight percent solids, heating the slurry with stirring to 85° to 95° C., maintaining the slurry at 85° to 95° C. with stirring for 10 to 15 minutes until the dispersion of the solid material is complete, cooling the dispersion to 70° C. adjusting the pH of the dispersion to 4.3 to 4.5 and then spray drying and collecting the finely-divided dried solidified product.

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